

## RAW MATERIALS

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### DIATOMITE — SILICEOUS MATERIAL FOR THE GLASS INDUSTRY

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The chemical-mineralogical determination and physical properties of the sedimentary rock diatomite are examined. The results of x-ray phase, differential thermal, thermogravimetric, and infrared spectroscopic analyses of diatomite from the Inzenskoe deposit are presented. The results of experimental production of glass granules based on diatomite are described.

**Key words:** diatomite, amorphous silica, opal-cristobalite rock, microporous structure, density, granulometric composition, moisture content.

The glass industry is one of the biggest users of raw materials containing silica. The reserves of high-quality naturally occurring silica raw material from explored deposits, specifically quartz glass sands, are limited and distributed nonuniformly in the Russian Federation, while at the same time the rates of growth of the glass industry are running substantially ahead of the development of the corresponding raw-materials sector of the economy [1]. All this shows a need to develop new deposits of raw materials for glass production, improve the materials-technological base of mining-enrichment combines and works and expand the raw materials base of the glass industry.

In the Russian Federation the Tashlinskii (Ul'yanovsk Oblast), Ramenskii (Moscow Oblast) and the Nebolchinskii Mining-Enrichment Combines as well as the Maraevnya (Ryazan Oblast) and Anotovskaya (Amurskaya Oblast) enrichments factories produce enriched quartz sands and concentrates. According to the Federal State Unitary Enterprise Central Scientific-Research Institute of the Geology of Non-Metallic Minerals, the volume of production of quartz glass sands in the Russian Federation in 2008 was  $3.22 \times 10^6$  tons (including  $2.17 \times 10^6$  tons enriched sands)

while the demand during this period was  $6.82 \times 10^6$  tons. Thus, the shortfall reaches  $3.6 \times 10^6$  tons and is made up by imports, according to data from the VVS company [2].

For the glass industry high-silica amorphous rocks (opal-cristobalite rocks) are of great interest as an alternative source of siliceous raw material, specifically, quartz sand. These rocks include diatomites, opokas, tripolis, obsidians, perlites, pichstones, spongolites, and radiolarites. The main advantage of opal-cristobalite raw material is the high content of the amorphous phase of silicon dioxide (to 70% amorphous  $\text{SiO}_2$ ). The biogenic structure of silica in opal-cristobalite rocks is due to anomalous properties as compared with artificially obtained amorphous silicon dioxide and fine-crystalline quartz. For this reason, even though silicon has a high oxygen affinity the melting temperature of silica from opal-cristobalite rock is lower ( $1500 - 1550^\circ\text{C}$ ) than that of quartz ( $1713 - 1728^\circ\text{C}$ ), and this makes it possible to lower the glassmaking temperature. Another important advantage of this raw material is that it contains other glass-forming and modifying oxides, which makes it possible to decrease the use of expensive components of the glass batch and therefore lower the cost of production of the finished articles.

Of all the representatives of the opal-cristobalite group diatomites are considered to be the most promising raw material for the glass industry because they have the most stable chemical-mineralogical composition, which is due to the specific conditions under which they are formed.

Diatomite is a loose earthy or weakly cemented, porous and light-weight sedimentary rock, formed mainly by the si-

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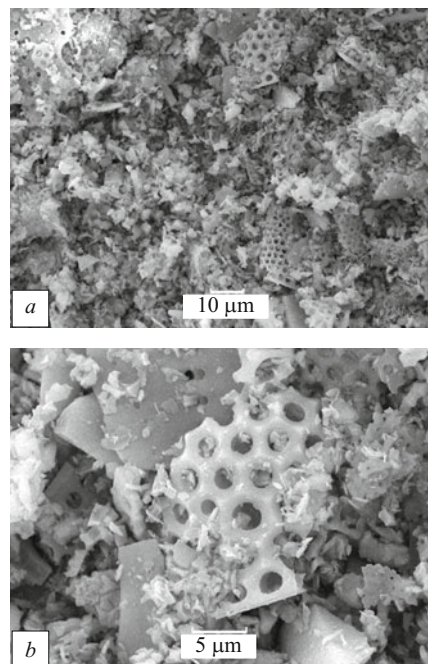
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siliceous fragments of shells (skeletons) of diatomaceous algae — diatoms and radiolaria. The siliceous shell (skeleton) consist mainly of silica hydrates of various degrees — opals of the form  $m\text{SiO}_2 \cdot n\text{H}_2\text{O}$ .

Lacustrine diatomites are comprised mainly of whole frustules of diatomite algae, while broken frustules predominate in marine rocks. The content of whole frustules can serve as a quality indicator for diatomites, but this rule may not stand up because their size varies over a wide range. Figure 1 contains photographs obtained with a Jeol JSM-6480LV scanning electron microscope with a tungsten thermionic cathode and ultrathin ATW-2 window (resolution 129 eV on  $\text{K}_\alpha$  Mn) in the Laboratory for Local Methods of Studying Matter in the Department of Geology at Moscow State University. Figure 1a shows a photograph of diatomite dried a  $250^\circ\text{C}$ ; diatom skeletons and broken diatom particles are clearly visible and particles differing from diatom skeletons of diatoms and representing foreign minerals present in diatomite can also be distinguished. Figure 1b clearly shows that the sizes of pores in diatom skeletons of diatoms range from several microns to less than  $1\ \mu\text{m}$ . Thus, diatomites possess the microporous structure of shells-particles of diatom algae, which increases considerably the interior surface area of the material and, correspondingly, the reaction surface.

Diatomites are white, yellowish-grey, light-grey and sometimes dark-grey and brownish-grey. The dark and brown color of diatomites is due to the presence of organic impurities, including plant residues. The yellowish-grey and yellowish-brown colors are due to the presence of free iron oxides [3].

Russia possesses many deposits of diatomites differing with respect to chemical composition (content of oxides).

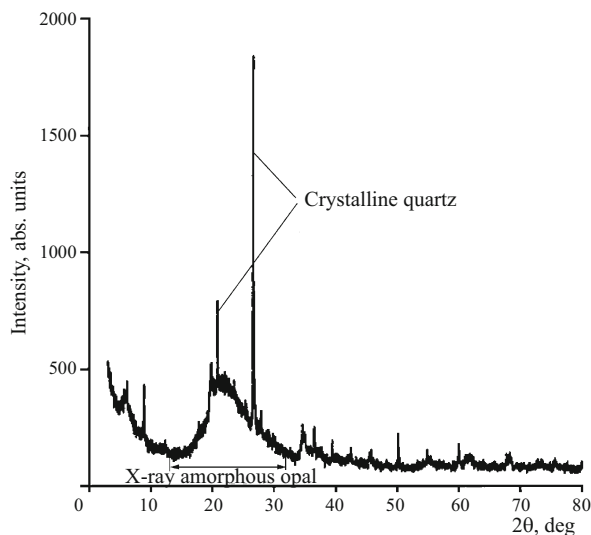


**Fig. 1.** Photographs of diatomite, obtained with a scanning electron microscope.

The chemical compositions of some of them are presented in Table 1. The chemical compositions of quartz glass sand from several deposits and diatomite from the Inzenskoe deposit are compared in Table 2. On the basis of the data in Tables 1 and 2 it can be asserted that the silica content in diatomite is close to that of quartz sand and the compositions have nearly the same content of alkali oxides; a high content of a clayey fraction is present in diatomite.

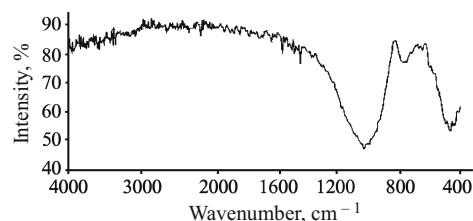
**TABLE 1.** Chemical Composition of Diatomites from Several Deposits in Russia

Deposit	Location	Content in dry rock, wt.%								
		$\text{SiO}_2$	$\text{Al}_2\text{O}_3 + \text{TiO}_2$	$\text{Fe}_2\text{O}_3 + \text{FeO}$	CaO	MgO	$\text{K}_2\text{O}$	$\text{Na}_2\text{O}$	$\text{SO}_3$	other
Inzenskoe	Ul'yanovsk Oblast	74.8 – 88.1	3.3 – 9.7	2.3 – 5.2	0.6	0.6 – 1.7	0.96	0.74	–	2.7 – 5.8
Zabaluiskoe	Ul'yanovsk Oblast	83.71	5.69	2.05	0.49	0.73	0.42	0.19	–	6.6
Sengileevskoe	Ul'yanovsk Oblast	81 – 86.4	5.3 – 7.95	1 – 3.38	0.6	0.7 – 1.1	0.42	0.4	–	4 – 6.8
Balasheiskoe	Samara Oblast	78.55	8.68	4.34	0.57	0.83	–	–	–	6.6
Atemarskoe	Mordoviya	77 – 85.8	4.8 – 9.8	2.3 – 3.9	0.2 – 1.2	0.6 – 1.3	–	1.3	0.62	5.0
Irbitskoe	Sverdlovsk Oblast	72 – 79.5	6.8 – 10.45	2.87 – 5.94	0.2 – 0.9	1 – 1.3	1.1	0.4	0.25	6.5
Kamyshlovskoe	Sverdlovsk Oblast	76.6 – 78.2	6.5 – 7.8	2.79 – 3.26	0.7 – 1	1 – 1.7	1.3	0.3	–	11.0
Potaninskoe	Chelyabinsk Oblast	75.6 – 77.6	7.9	3.98	0.75	1.4	1.2	0.5	1.13	6.7 – 7.5
Millerovskoe	Rostov Oblast	75.75	7.55	4.41	1.84	1.0	1.65	0.27	–	6.29
Shibikskoe	Krasnodarskii Krai	65 – 76	4.6 – 18	0.5 – 4.4	1 – 5	0.1 – 1	–	3.3	0.8	4 – 7
Pionerskoe	Primorskii Krai	63 – 80.5	12.3 – 22.9	2.2 – 9	1.0	0.4 – 1.3	1.5	0.75	0.4	2 – 6
Kovdozero	Murmansk Oblast	65.5	3.89	1.48	1.8	0.94	–	–	–	5.4
Lumbolka	Murmansk Oblast	67.0	7.24	2.37	2.49	1.4	–	–	–	24.6
Nyudozero	Murmansk Oblast	71.7	5.23	1.86	1.73	1.34	–	–	–	17.2
Kallivere	Leningrad Oblast	64 – 79.85	1 – 11.4	4.0 – 4.91	1.4 – 2.7	0.7 – 1.8	–	–	1 – 3.7	4 – 13.8



**Fig. 2.** X-ray phase analysis of diatomite from the Inzenskoe deposit (ARL X'TRA x-ray diffractometer, Scientific-Technical Center for Silicate Materials and Technology, Inza).

X-ray phase analysis of diatomite showed that the amorphous component of diatomite is represented by a variety of opal. This is expressed by diffraction reflections with diffuse peaks at small and medium angles in the x-ray diffraction pattern presented in Fig. 2; the crystalline component is represented by quartz impurity. Most of the diatomite samples which have been studied (Paleogene of Povolozh'e, Eocene of Trans-Urals, Miocene of Trans-Caucasia and Moldova, Holocene of the Kola Peninsula and others) usually do not contain even traces of cristobalite. Weak reflections due to cristobalite are seen only in individual samples [4]. The clayey component in diatomites is represented by montmorillonite, beidellite, kaolinite, and hydromicas. Usually, minerals of the montmorillonite group predominate. Montmorillonite (often poorly crystallized) is typical for diatomites of Trans-Caucasia and diatomites and tuff-diatomites of Sakhalin, and it is one of the main clayey minerals of diatomites of Trans-Urals and Povolozh'e. The mass fraction of



**Fig. 3.** IR spectrum of diatomite from the Inzenskoe deposit (Specord M80 spectrophotometer, D. I. Mendeleev Russian Chemical Technology University, sample — KBr pellet, diatomite content 1 wt.%).

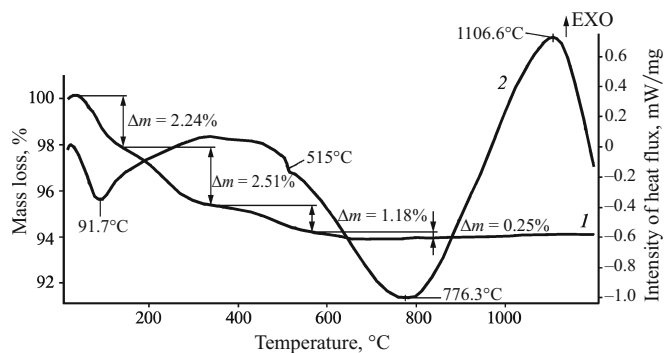
the amorphous phase in the diatomite from the Inzenskoe deposit is 73%,<sup>5</sup> the crystalline quartz content is only 6%, montmorillonite  $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$  10%, ordinary mica  $\text{KMgAlSi}_4\text{O}_{10}(\text{OH})_2$  7%, feldspar  $\text{KAlSi}_3\text{O}_8$  1%, and other impurities 3%.

Infrared spectroscopic analysis of diatomite from the Inzenskoe deposit showed that the silicates in diatomite are comprised of metasilicate chains and silicate rings (Fig. 3). The weak peaks indicate metal impurities with weak covalent bonds, for example, Na, K and others. Fluctuations of the background are observed at frequencies above  $1400\text{ cm}^{-1}$ . The peaks in the frequency range  $3000 - 4000\text{ cm}^{-1}$  show negligible absorption with no distinct maxima and are determined by the presence of stretching vibrations of water  $\nu(\text{OH})$ . Using this spectrogram it is impossible to identify the residue to which this water refers — alkaline or acidic. The deformation vibrations  $\delta(\text{OH})$  at the frequencies 1576 and  $1568\text{ cm}^{-1}$  also attest to the presence of water in the structure. It is believed that the peaks at frequencies to  $1650\text{ cm}^{-1}$  indicate the presence of whole water molecules in the composition; they could also be associated with OH groups, while at the frequencies of peaks above  $1650\text{ cm}^{-1}$  acidic water is present, i.e., water bound with acidic centers (for example, Si). Peaks of average intensity in the frequency range  $400 - 620\text{ cm}^{-1}$  attest to the presence of deformation vibra-

<sup>5</sup> Here and below the content by weight.

**TABLE 2.** Average Chemical Composition of Quartz Sand and Diatomite

Raw material (deposit)	Content, wt.%							
	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{CaO}$	$\text{MgO}$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	Other
Quartz sand (Gekmalinskoe)	83.27	2.90	1.87	4.38	—	—	—	—
Quartz sand (Tashlinskoe)	98.81	0.44	0.06	0.37	0.20	—	—	—
Quartz sand (Sulutapinskoe)	92.50	1.69	0.85	—	—	—	—	—
Quartz sand (Yasamal'skoe)	81.12	3.74	1.33	5.33	0.93	0.56	0.55	$\text{SO}_3 - 0.11$ $\text{P}_2\text{O}_5 - 0.11$
Quartz sand (Eganovskoe)	98.62	0.46	0.05	0.24	0.11	—	—	—
Quartz sand (Tulunskoe)	95.40	2.50	0.20	0.90	0.43	—	—	—
Diatomite (Inzenskoe)	81.98	5.37	2.67	0.36	0.80	0.24	1.23	$\text{TiO}_2 - 0.50$ $\text{BaO} - 0.30$



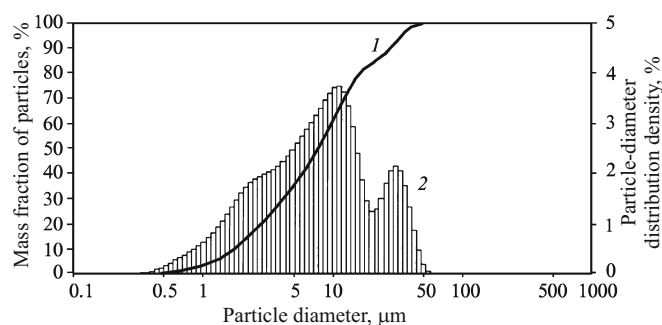
**Fig. 4.** DSC curve of diatomite from the Inzenskoe deposit [4]: 1) mass change  $\Delta m$ , %; 2) DSC curve.

tions of silicate bonds. Peaks of average intensity in the frequency range  $800 - 600 \text{ cm}^{-1}$  also correspond to silicates. The strong peak at  $1036 \text{ cm}^{-1}$  is due to stretching vibrations  $\nu(\text{Si-O-Si})$ , while the peak at  $468 \text{ cm}^{-1}$  is due to deformation vibrations  $\delta(\text{Si-O-Si})$ .

The behavior of material on heating is of great importance for determining the technological properties of diatomite. Comprehensive thermal analysis performed with a differential scanning calorimeter (O. V. Kaz'mina's data, Fig. 4, curve 2) identified two endo effects: at low temperature peaking at  $91.7^\circ\text{C}$  corresponding to the removal of adsorption water and at  $776.3^\circ\text{C}$  corresponding to a polymorphic transformation of quartz present in diatomite [5]. Thermogravimetric analysis attests to even, continual removal of adsorption and capillary-condensed water in micropores of amorphous silica, i.e., its degradation on heating to  $1200^\circ\text{C}$ ; in addition, most water (of the order of 80% of the total mass loss of 5–6%) is already removed at  $400^\circ\text{C}$  (Fig. 4, curve 1).

An important characteristic for the production technology is the particle-size composition of the raw material. It must be taken into account when the raw material is prepared, transported and mixed with other components, which ultimately influences the quality of the batch. Quarry diatomite contains large amounts of coarse inclusions and must be pre-comminuted. It is an easily comminuted material (rock) with Mohs hardness 2. Figure 5 displays the particle-size composition of comminuted quarry diatomite from the Inzenskoe deposit. The analysis was performed by diffraction on the CILAS 1064 apparatus (Analysette 22), which can be used to determine the dispersity of material in water (alcohol solution), and on the HELOS&RODOS apparatus, which makes it possible to analyze the particle size of material in dry form. The method of dry dispersing is preferable for analysis of the particle-size composition, since diatomite is hydrophilic. On the whole the particle-size distribution shows that particles several microns in size predominate in dry-comminuted diatomite; particles  $< 1 \mu\text{m}$  and several tens of microns in size are also present.

Aside from chemical-mineralogical determinations, physical properties such density, bulk density, strength, ther-



**Fig. 5.** Particle-size composition of comminuted diatomite (CILAS 1064 laser particle analyzer): 1) mass fraction of particles, %; 2) particle-diameter distribution density, %.

mal conductivity, angle of repose, caking, pelletizability and moisture content must be taken into account in order to evaluate the quality of diatomites and to develop a technology for producing different materials with use of diatomites.

The density of diatomites fluctuates over a substantial range from  $0.21$  to  $1 \text{ g/cm}^3$  or more [4] depending on the deposit. In addition, the higher the content of whole diatom frustules and their large fragments, the lower the density is. The light weight and looseness of diatomites are also due to the presence of faceting (usually more than 10% [4]). The main factor responsible for an increase of the density of diatomites is the presence of fragmented and clayey materials. The average density of fragmentary diatomites from the Inzenskoe deposit is  $0.68 \text{ g/cm}^3$  and that of diatomites in the form of powder  $0.27 \text{ g/cm}^3$ .

Moisture plays a special role in the evaluation of the physical parameters of diatomites, especially if the diatom structure, which permits water to enter diatoms and be trapped, is taken into account. The moisture content determines many technological parameters of diatomites, such as the bulk density, friability, caking, plasticity and others. Thus, the values of many physical properties are associated with the moisture content of diatomite. The natural diatomite from the quarry in the Inzenskoe deposit is a coarse-fragmentary material with moisture content 47–50%, and after grinding it is a dark-grey plastic mass with slightly lower moisture content because of water evaporation from the surface.

Two properties of greatest importance for technology are the bulk density and angle of repose of the material. The bulk density determines the volume occupied by the material in a hopper. For diatomite from the Inzenskoe deposit the dependence obtained shows that the bulk density depends strongly on the moisture content of diatomite; this dependence is nonlinear and varies from  $0.35$  to  $0.59 \text{ g/cm}^3$  for moisture content from 7.3 to 50.0%, respectively. Evidently, the bulk density of diatomite is about  $0.35 \text{ g/cm}^3$  in a wide range of moisture content from 5 to 35%, and as the moisture content increases the bulk density starts to increase linearly at first and then more rapidly [6].

Another important characteristic for technology is the angle of repose formed by freely poured material. This angle is uniquely related with properties of the material such as friability, which is very important for transport, storage, mixing and other technological operations. The angle of repose also depends strongly on the moisture content of diatomite: the higher the moisture content, the larger the angle of repose and, correspondingly, the lower the friability of diatomite.

In analyzing diatomite from the Inzenskoe deposit the dynamic angle of repose was studied following GOST 27802–93. Depending on the moisture content the dynamic angle of repose varied from 30 to 44°. Three characteristic sections can be singled out: from 5 to 20% moisture content the angle of repose increases sharply from 30 to 40° and remains practically constant from 20 to 40%, above which it increases evenly.

Plasticity is the capability of diatomite to form when mixed with water dough which under external forces can acquire any shape without loss of continuity and retain its shape after the forces are removed. The plasticity of diatomites depends on the particle-size and mineralogical compositions of diatomites [7]. As particle-size increases, the plasticity of diatomite increases. High plasticity is characteristic of quarry diatomite from the Inzenskoe deposit.

In evaluating the quality of siliceous rock as fillers for light-weight concretes, granular filtration materials and desiccators the mechanical stability against external perturbations is important. The compression strength of diatomites is relatively low and varies in the range 0.7 – 3.5 MPa depending on the deposit. For diatomites from the Inzenskoe deposit the average compression strength is 3.34 MPa.

An important property of diatomites is thermal conductivity. Diatomites are characterized by high heat-insulation properties; their thermal conductivity fluctuates from 0.0465 to 0.1233 W/(m · K). The thermal conductivity of diatomites from the Inzenskoe deposit is 0.092 – 0.098 W/(m · K).

Experimental production of glass granules based on diatomite raw material with composition close to that of VVS window glass at the enterprise Nikol'skii Light-Engineering Glass Plant JSC showed that the melting temperature can be reduced considerably. Melting was conducted in the tank of a horseshoe, batch, glassmaking furnace; the melting tempera-

ture was 1430°C. Three meltings with mass 60 kg in each one were conducted. Visually, the glass obtained was completely melted and fined, the glass color was intense green transitioning into olive. The glass granules obtained can be used, among other purpose, to obtain high-quality foamed glass by the powder technology. Diatomite is less expensive than quartz glass sand, which makes it possible to decrease the production costs of batch and the final product itself, while lowering the melting temperature as a result of the structural and compositional particulars of diatomite, including its microporosity and degree of hydration, makes it possible to considerably decrease energy consumption in the production process, increase the service life of the furnace and, correspondingly, lower the production costs of the finished product. Studies of diatomite and experimental melting of batch based on it have shown that it holds promised for use in the glass industry as a complete or partial substitute for quartz sand, which is in short supply, in the production of glass granules, foamed glass and other forms of glass.

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